

SUMMARY OF RESEARCH  
(ANNUAL STATUS REPORT)

NASA Research Cooperative agreement: NCC-1-02030

“High Performance Polymers”

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## INTRODUCTION

This report summarizes results obtained from research funded through Research Collaboration Agreement No. NCC-1-02030, "High Performance Polymers." Results are reported in three of the proposed research areas (Tasks 1-3 in the original proposal):

- Effort to improve the synthesis and to understand and replicate the dielectric behavior of 6HC17-PEK.
- Continue preparation and evaluation of flexible, low dielectric silicon – and fluorine – containing polymers with improved toughness.
- Synthesis and characterization of high performance polymers containing the spirodilactam moiety.

## RESULTS

- Effort to improve the synthesis and to understand and replicate the dielectric behavior of 6HC17-PEK.

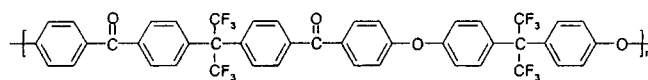
Considerable progress was made in our understanding and ability to replicate the unique dielectric behavior observed when films of the polyetherketone, 6HC17-PEK, are cast from selected mixed solvents. Several points now seem clear. The white opaque film of 6HC17-PEK has been reproduced (dielectric constant=1.80 at 10GHz vs ~2.5 for film cast from pure  $\text{CHCl}_3$ ) by casting from the mixed solvent,  $\text{CHCl}_3$  and isobutyl alcohol. It also now appears that the non-solvent must be less volatile than the solvent and that the observed phenomenon is quite a general one for many types of polymers (Table 1). The effect of solvent /non-solvent relative volatilities is readily seen by comparing the dielectric constants of Film 1 to 2 and 3 or Film 8 to 9 and 10. Films 3 and 10 which exhibit dielectric constants which are essentially identical to the

controls (1 and 8) were cast from toluene/methanol mixtures. These films are not opaque but rather are clear and look like controls obtained from the pure solvents. Films 2 and 9 which were cast from  $\text{CHCl}_3$ /isobutyl alcohol mixtures are opaque and have the lowered dielectric constants.

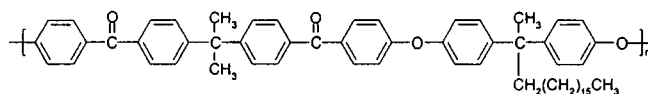
**Table 1. Preparation condition and dielectric constant of polymer films**

Film No.	Polymer	Solvent system	Drying condition	Dielectric constant
1	12F-PEK	Chloroform	I	2.79
2	12F-PEK	Chloroform/isobutyl alcohol	I	1.80
3	12F-PEK	Toluene/methanol	I	2.68
4	12F-PEK	Chloroform/isobutyl alcohol	II	1.86
5	12F-PEK	Chloroform/2-propanol	I	1.93
6	C <sub>17</sub> -6H-PEK	Chloroform/DMAc	I	2.38
7	C <sub>17</sub> -6H-PEK	Chloroform/isobutyl alcohol	I	1.80
8	Polyimide	Chloroform	I	2.74
9	Polyimide	Chloroform/isobutyl alcohol	I	2.24
10	Polyimide	Toluene/methanol	I	2.67
11	Polyimide	Chloroform/isobutyl alcohol	II	2.05

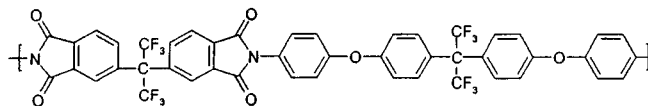
I- the film was dried for 8 hours at 40°C, II- the films were further dried for an additional 26 hours at 150°C *in vacuo*.



12F-PEK



C<sub>17</sub>-6H-PEK



Polyimide

The phenomenon being observed appears to be related to microphase separation which occurs as the more volatile polymer solvent evaporates at a faster rate than the less volatile non-solvent. This is a known phenomenon which has been exploited in the preparation of membranes. Scanning electron micrographs suggest that the low dielectric films do contain micropores as might be anticipated if microphase separation is the operative phenomenon.

- Continue preparation and evaluation of flexible, low dielectric silicon – and fluorine – containing polymers with improved toughness

[illegible]

### Scheme 1. Synthesis of Polymers

As outlined in Scheme 1, a polymer capable of hydrolytic crosslinking and /or hyperbranching was prepared from a monomer mixture containing 10 mol-percent of divinyltetraethoxydisiloxane. Earlier work at a 5 mol-percent loading of this crosslinking monomer had provided in one instance a polymer ( $M_w = 24 \times 10^3$ ,  $PD = 2.4$ ,  $T_g = -61^\circ$ ) which underwent hydrolysis and thermal curing ( $135^\circ\text{C}$ , 48h., in vacuo) to give a product ( $M_w = 113 \times 10^3$ ,  $PD = 9.0$ ,  $T_g = -60^\circ$ ). Of some significance, the  $T_g$  value remained essentially unchanged even though the  $M_w$  increased about five-fold and the  $PD$  value almost quadrupled, and, most important, the polymer remained soluble. This observation suggests that the increased molecular weight resulted primarily from hyperbranching rather than crosslinking. In another experiment involving a 5 mol-percent loading of the crosslinking monomer the initially obtained product ( $M_w = 41 \times 10^3$ ,  $PD = 3.0$ ,  $T_g = -63^\circ$ ) was only partially soluble after hydrolysis and thermal cure but retained a  $T_g$  of  $-59^\circ$ . These results suggested that more extensive crosslinking had occurred in this experiment.

In order to gain further insight into these interesting but somewhat contradictory results, the experiment at 10 mol-percent crosslinker described in Scheme 1 was performed. The soluble product was then hydrolyzed and thermally cured. The weight-average molecular weight,  $M_w$ , polydispersity,  $PD$ , and glass transition,  $T_g$ , were then monitored as function of cure time (Figures, 1-3). As shown in Figures 1 and 2, the  $M_w$  and  $PD$  values increase with cure time as anticipated, but the curves appear to experience a change of slope after about 120h, and the polymer ( $M_w \sim 220 \times 10^3$ ,  $PD \sim 23$ ) remains soluble in THF after 10 days of cure. The glass transition remains essentially constant at about  $-60^\circ$ . Once again, the results suggest that hyperbranching, not crosslinking, is the operative phenomenon leading to the increase in  $M_w$ . Additional work on this project is suggested.

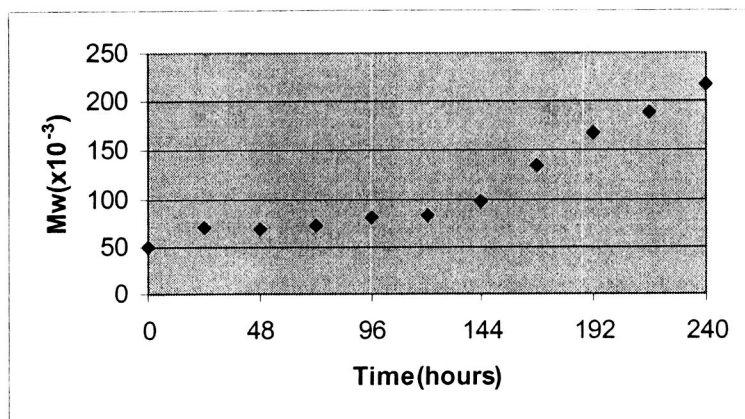


Figure 1.  $M_w$  vs Time

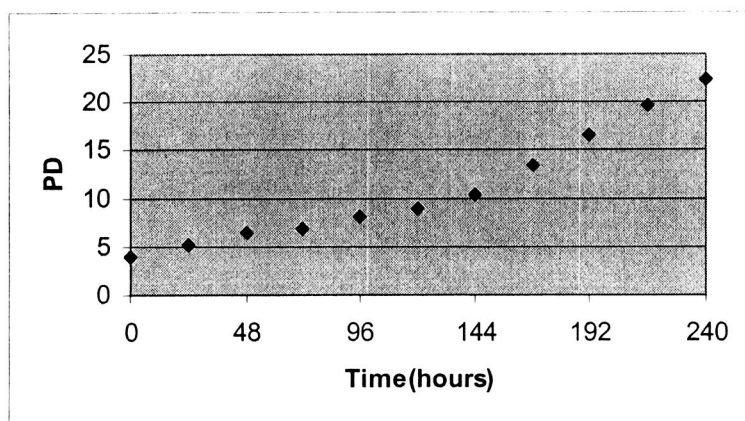


Figure 2. PD vs Time

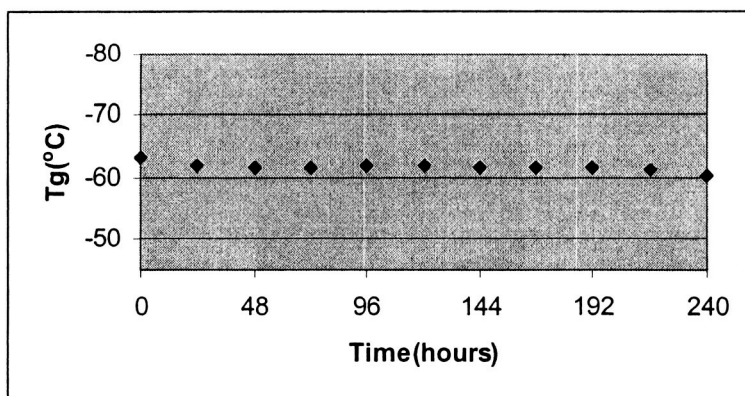
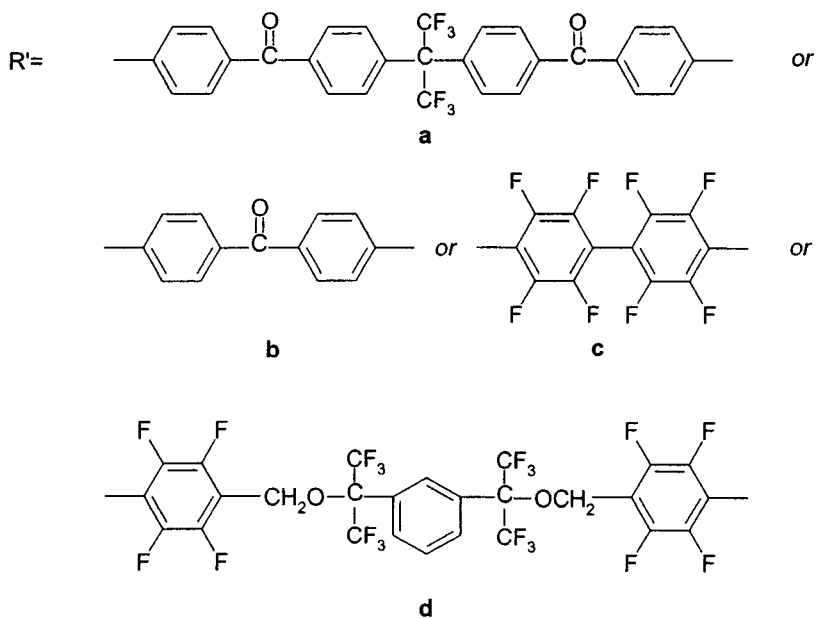
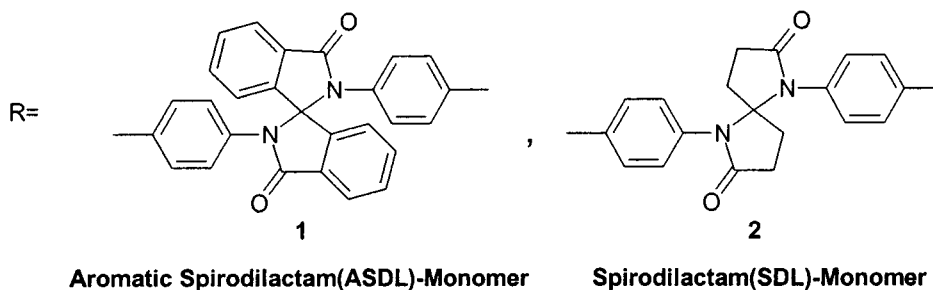
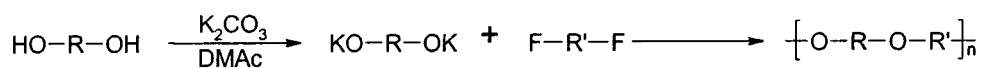


Figure 3.  $T_g$  vs Time

- Synthesis and characterization of performance polymers containing the spirodilactam moiety

A series of new polyethers containing the spirodilactam moiety as a backbone component has been prepared and characterized. The polymerizations were performed using the standard techniques of reaction of diphenol with an activated difluoromonomer (Scheme 2). Thus, for



### Scheme 2 SDL and ASDL Polymer Synthesis

example, reaction of an aromatic spirodilactam diphenol with 4, 4'-difluorobenzophenone ( $R'=b$ ) would yield a polyether labeled **1-b**. The properties of the polymers obtained are tabulated in Tables 2 and 3. The ASDL polymers (Table 2), especially **1-a** and **1-b**, have quite exceptional thermal properties. Dielectric properties are minimized in polymers **1-d** and **2-d** as might have been anticipated from structure of the active fluoro-monomer used. Finally, it is noted that polymers **1-a, b** and **c** and **2-a, b** and **c** have rather high Tg values (as would be predicted from the more rigid  $R'$  moieties), which may be desirable for some applications.

**Table 2. Properties of Spirodilactam diphenol-derived PEK's prepared from monomer 1 and selected difluoro-monomers**

Property		1-a	1-b	1-c	1-d
$\eta_{inh}$ (dL/g) ( $CHCl_3$ )		0.43	0.20	0.23	0.29
$M_w^a \times 10^{-3}$		59.8	35.5	655.7	--
Polydispersity		1.6	1.5	13.2	--
$T_g^b$ ( $^{\circ}C$ )		240	255	279	167
TGA <sup>c</sup> ( $^{\circ}C$ 10% wt loss)	Air	595	618	499	409
	Argon	598	613	501	474
% Char Yield (@800 $^{\circ}C$ )	Air	17	40	1	36
	Argon	66	67	51	38
Dielectric Constant (10GHz)		2.80	3.00	2.72	2.54
Percent H <sub>2</sub> O Absorption		1.2	1.9	1.2	nil

<sup>a</sup>: Measured by GPC; <sup>b</sup> Measured by DSC at 10  $^{\circ}C/min$ ; <sup>c</sup> Measured at 20  $^{\circ}C/min$ .

**Table 3. Properties of Spirodilactam diphenol-derived PEK's prepared from monomer 2 and selected difluoro-monomers**

Polymer		2-a	2-b	2-c	2-d
$\eta_{inh}$ (dL/g) ( $CHCl_3$ )		1.03	0.71	0.40	0.28
$M_w^a \times 10^{-3}$		613.2	--	64.6	43.1
Polydispersity		7.8	--	1.9	1.9
$T_g^b$ ( $^{\circ}C$ )		243	261(232) <sup>d</sup>	276	161
TGA <sup>c</sup> ( $^{\circ}C$ 10% wt loss)	Air	533	471	416	400
	Argon	510	458	443	409
% Char Yield (@800 $^{\circ}C$ )	Air	1	4	2	2
	Argon	60	56	44	36
Dielectric Constant (10GHz)		2.74	2.93	2.67	2.53
Percent H <sub>2</sub> O Absorption		2.1	3.6	3.1	nil

<sup>a</sup>: Measured by GPC; <sup>b</sup> Measured by DSC at 10  $^{\circ}C/min$ ; <sup>c</sup> Measured at 20  $^{\circ}C/min$ ,

<sup>d</sup> P.C. Wang, U.S. Pat. 5049640, 1991



## **INVENTIONS:**

### **Presentations/Publications:**

1. Fitch, J.W.; Bucio, E.; Martinez, L.; Macossay, J.; Venumbaka, S.R.; Dean, N. and Cassidy, P.E. "Synthesis and Characterization of New Fluorine-containing Polyethers" *Polymer*, in press.
2. Bucio, E.; Fitch, J.W.; Martinez, L.; Venumbaka, S.R. and Cassidy, P.E. "Synthesis and Properties of Aliphatic Spirodilactam Diphenol Containing Polyesters" *Polymer Preprints*, **2003**, 44(1), 835.
3. Zhou, H.; Mannari, V.; Venumbaka, S.R.; Fitch, J.W. and Cassidy, P.E. "A Facile Method for Preparation of Ultralow Dielectric Constant Polymer Films" *Polymer Preprints*, **2003**, 44(1), 884.
4. Cassidy, P.E.; Fitch, J.W. and Venumbaka, S.R. "New Step-Growth Fluoro Polymers" Paper presented at *Fluoropolymer 2002* conference, Savannah, Georgia, October **2002**.
5. Zhou, H.; Venumbaka, S.R.; Fitch, J.W. and Cassidy, P.E. "Novel High Performance Polymers Derived from Aromatic and Aliphatic Spirodilactam Diphenol" *Polymer Preprints*, **2002**, 43(2), 1347.

### **Patents:**

1. Cassidy, P.E.; Fitch, J.W.; Stoakley, D.M.; Mannari, V.M.; Venumbaka, S.R. and Zhou, H. "Void-containing, Low Dielectric Films by Multiple Solvent Evaporation" October **2002**, Submitted Provisional Application for US Patent.

## **INVENTORY:**

No major equipment was purchased during this grant period.